

PATENT SPECIFICATION

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DRAWINGS ATTACHED

- (21) Application No. 5718/68 (22) Filed 5 Feb. 1968
(31) Convention Application No. 614 338 (32) Filed 6 Feb. 1967 in
(33) United States of America (US)
(45) Complete Specification published 25 Nov. 1970
(51) International Classification C 07 c 21/06
(52) Index at acceptance

C2C 1G1A2 1G1B2 1G1C2X 1G1D 1G1E 1G6A1 1G6A2
1G6B6
B1E 320 322 32Y 330 331 33Y 350 35Y 362 36Y 491 49Y
515 521 526 591 612 640 642 648



(54) PROCESS FOR THE PRODUCTION OF VINYL CHLORIDE

(71) We, THE LUMMUS COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of 1515, Broad Street, 5 Bloomfield, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

chlorinated hydrocarbons from ethane and hydrogen chloride using a molten chloride salt; a large amount of hydrogen chloride is also formed which must be recovered and recycled for economic reasons. In the known 50 process, this hydrogen chloride is recovered from the product stream and recycled to the oxidation reactor. This method has a disadvantage in that hydrogen chloride recovery requires costly equipment resistant to hydro- 55 choric acid, and further requires extensive quantities of steam and cooling water as utilities. Furthermore, this known process produces vinyl chloride and large quantities

This invention relates to the production of vinyl chloride, especially using ethane, ethylene or mixtures thereof as starting materials.
15 Vinyl chloride is generally produced from ethylene and chlorine feeds. Chlorine is contacted with ethylene at temperatures of from about 100°F. to 300°F., perhaps in the presence of a catalyst, to form a 1,2-dichloro-
20 ethane intermediate. The dichloroethane intermediate is then dehydrochlorinated catalytically at a temperature of from about 700°F. to 1000°F. to form vinyl chloride and hydrogen chloride.

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25 The commercial feasibility of this method depends on the economic recovery of the hydrogen chloride which is produced. One technique is to react the hydrogen chloride with acetylene to produce vinyl chloride.
30 Alternatively, the hydrogen chloride is used to produce more dichloroethane intermediate which is then dehydrochlorinated to produce vinyl chloride. According to this method, ethylene, hydro-
35 gen chloride and oxygen are contacted at about 500°F. to 700°F. over a copper chloride-based catalyst in either a fixed bed or fluidized bed reactor. The reaction is exothermic and, consequently, heat must be
40 removed from the reaction apparatus.

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The present invention utilizes a molten salt catalyst, which can serve as chlorine transfer medium, oxygen transfer medium, or heat transfer medium.

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45 A process is known for the production of
[Price 5s. Od. (25p)]

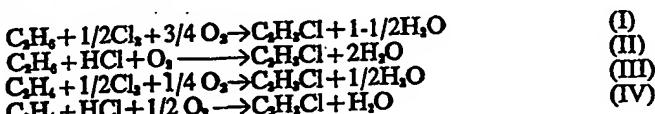
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ing a chloride of the said metal in a second reaction zone wherein 1,2-dichloroethane is dehydrochlorinated to produce an effluent containing vinyl chloride and separating 5 vinyl chloride as product therefrom. Oxygenation of the mixture of chlorides of the metal in at least a higher and a lower valence state (e.g. a mixture of cupric chloride and cuprous chloride) gives rise to 10 a product which contains the oxychloride of the metal (e.g. copper oxychloride by the reaction of $2 \text{CuCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{CuO} \cdot \text{CuCl}_2$). This oxychloride in the chlorination stage reacts with hydrogen chloride added to or 15 generated in the first reaction zone (the chlorinating zone) to produce the chloride of the metal in a higher valence state (e.g. cupric chloride). The higher valent chloride trans-

fers chlorine to the organic components of the gaseous feed and is itself converted to 20 a hot product containing the chloride of the metal in its lower valence state (e.g. cuprous chloride).

In the preferred form of the process, the hot melt formed in the first zone is supplied 25 primarily as the catalyst to the second zone; it promotes the dehydrochlorination reaction and also gives up the heat generated in the first zone, for the reaction in the second zone is endothermic.

The overall reactions for the conversion of ethane and/or ethylene to vinyl chloride by reaction with oxygen, chlorine and/or hydrogen chloride according to the invention are represented by the following equations:



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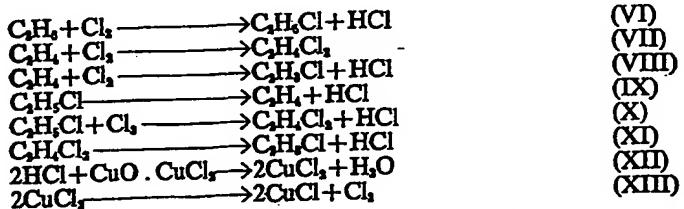
The introduction of oxygen into a molten halide salt by contact between the salt and a gas containing molecular oxygen can be

represented by Equation V which represents a molten salt system containing copper 45 chloride



The primary reactions which can occur in the process are represented by the following 50 equations:

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The chlorine which may be present in the feed and also that which is generated from the higher valent metal chloride in the molten salt, as represented by Equation XIII (in which the metal chloride is cupric chloride) chlorinates the ethane, ethylene and ethyl chloride with the concurrent production of hydrogen chloride as represented by Equations VI, VIII and X. Chlorinated hydrocarbons (ethyl chloride and dichloroethane) are dehydrochlorinated to form ethylene or 60 a chlorinated hydrocarbon and concurrently hydrogen chloride as represented by Equations IX and XI. The hydrogen chloride generated by these chlorination and dehydrochlorination reactions together with any 65 hydrogen chlorine feed reacts with the metal oxychloride in the molten mass to form water and the higher valent metal chloride as represented by Equation XII (in which the oxychloride is copper oxychloride). The 70 higher valent metal chloride is reduced to

the lower valence state concurrently releasing chlorine, as represented by Equation XIII, or through direct reaction with a hydrocarbon or a chlorinated hydrocarbon.

While it is assumed that the foregoing explanation of the reactions and the equations set forth correctly describes the process of this invention, it is understood that other reactions may occur in the process of the invention.

It is seen from Equation I that for an ethane/chlorine fresh feed, stoichiometrically 0.5 moles of chlorine and 0.75 moles of oxygen are required per mole of ethane. Thus, if the oxygen is conveyed in the molten halide salt as copper oxychloride ($\text{CuO} \cdot \text{CuCl}_2$), at least 1.5 moles of copper oxychloride are needed per mole of ethane. The presence of ethylene in the ethane feed reduces the requirement of the metal oxychloride per volume of hydrocarbon feed as can be seen from Equation III. The pre-

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sence of hydrogen chloride in the chlorine feed increases the requirement for metal oxychloride as illustrated by Equation II and IV. When the aliphatic hydrocarbon in the 5 gaseous feed is ethane or a mixture of ethane and ethylene, the gaseous effluent withdrawn from the first reaction zone comprises vinyl chloride, ethylene, ethyl chloride and dichloroethane as well as unreacted feed components. When the aliphatic hydrocarbon is 10 ethylene, the gaseous effluent withdrawn from the first reaction zone comprises vinyl chloride, ethyl chloride and dichloroethane as well as unreacted feed components.

15 The molten chloride salt is formed from a multivalent metal chloride mixture. In the case of multivalent metal chlorides having inconveniently high melting points, such as cupric chloride, a metal chloride which is 20 non-volatile and resistant to the action of oxygen under the process conditions is added to the higher valent metal chloride to form a molten salt mixture of reduced melting point and volatility. Such metal chlorides 25 will be present in the melt with the metal in only a single valency state and are preferably alkali metal chlorides, especially potassium and lithium chlorides, but other metal chlorides and mixtures thereof, such as the 30 heavy metal chlorides, e.g. zinc, silver and thallium chloride, may also be employed. The metal chlorides are generally added to the multivalent metal chlorides in an amount sufficient to adjust the melting point of the 35 molten salt mixture to a temperature of about 500°F., and in the case of a salt mixture of copper chloride and potassium chloride, the potassium chloride content is in the range 20% to 40% by weight. It is to be understood, however, that in some cases the catalyst salt mixture may have a melting point 40 higher than 500°F., provided that the catalyst salt mixture remains in the form of a melt throughout the processing steps.

45 In the accompanying drawings:

Figure 1 illustrates a reactor system in accordance with this invention; and

Figure 2 illustrates the separation system in accordance with this invention.

50 We describe next the process shown in Figure 1, and for simplicity refer to copper as the metal having both a higher and a lower valence state. Referring now to Figure 1, a molten cuprous/cupric chloride 55 at a temperature of from 600° to 900°F. is introduced through line 10 into the top of a substantially vertical oxidation vessel 11 maintained at a pressure of from 1 to 20 atms. A compressed gas containing molecular oxygen, such as air, in line 105 is introduced into the bottom of vessel 11 and is passed in countercurrent contact to the descending molten salt. The vessel 11 may be provided with one or more sections of packing, generally indicated as 12, to promote in-

timate and effective contact between the compressed gas and molten salt. The molten salt is oxidized to produce oxychlorides, with the concurrent evolution of heat. The residence time of the molten salt within the 70 vessel 11 is from about 1 to about 60 seconds.

The effluent gas leaving the packing 12 (if present) near the top of vessel 11 is at a temperature of 600° to 900°F., and is contacted with a spray of quench liquid fed 75 through line 16 at a temperature of 200° to 400°F. The gas is cooled by such contact with the result that vaporized and entrained salts are condensed and eliminated from the gas stream. The quench liquid spray is concurrently vaporized and, together with the effluent gas, is withdrawn from the top of vessel 11. The total gaseous effluent is passed through line 17 to a cyclone separator 80 85 for the elimination of any solid material, which is returned to the vessel 11. The gaseous effluent is thereafter combined with another gaseous effluent in line 19 as more fully described below. The combined gaseous effluent is cooled to 100° to 150°F. in a heat 90 exchanger 21 to condense out the vaporized quench liquid, which is separated from the remaining gaseous effluent in a vapour/liquid separator 22. The quench liquid is passed through line 23 by a pump 95 24 to a heat exchanger 25 to cool the quench liquid to a temperature of about 100°F., with a portion being returned through line 16 to the upper portion of vessel 11. The gaseous effluent in separator 22 is 100 divided, one portion being passed through line 28 into a caustic scrubber 29. From the scrubber 29, inert gases, such as nitrogen introduced with the oxygen in the feed containing molecular oxygen are readily discharged from the reactor system.

The oxidized melt at a temperature of 700° to 1200°F. is withdrawn from the bottom of vessel 11 through line 13 by pump 14 and passed to the top of a reactor 15 110 which is also substantially vertical. The reactor 15 is operated at a temperature of 700° to 1200°F., at a pressure of from 1 to .20 atmospheres, and a residence time of 1 to 60 seconds. The reactor 15 is provided with sections of packing, generally indicated as 30, designed to effect intimate and effective contact between the gaseous feed components and the molten salt. Fresh feed hydrogen chloride, if any, and recycle ethyl 115 chloride, as more fully described below, at a temperature of from 100°F. to 200°F., are introduced into the upper portion of reactor 15 through line 31. Combined recycled ethane, ethylene and hydrogen chloride at a 120 temperature of 100° to 200°F. are introduced into reactor 15 through line 32 at a point below line 31. The introduction into reactor 15 of the recycle streams and the fresh 125 hydrogen chloride stream (if any) may be 130

further divided, reversed in position, or may be combined into one stream. In the first of these options, more entry ports into reactor 15 are required, so that there is one port 5 for each stream into reactor 15. In the second option, the fresh hydrogen chloride (if any) and recycle ethyl chloride are passed through line 32, while the recycle ethane, ethylene and hydrogen chloride are passed 10 through line 31. In the third option, the recycle streams and fresh hydrogen chloride (if any) are combined and enter the reactor 15 through line 31, line 32 being then unnecessary.

15 Fresh chlorine is introduced into reactor 15 through line 33 at a point below the recycle feed positions 31 and 32. Fresh feed ethane, ethylene, or mixtures thereof, is introduced through line 34 into reactor 15 in 20 the lower portion thereof. The hydrocarbon fresh feed in line 34 should be introduced at or near the bottom of the reactor 15 in order to fully extract all chlorine values added to the melt in reactor 15. In this 25 manner, the melt withdrawn from reactor 15 will be made essentially non-chlorinating under the process conditions prevailing in the dehydrochlorination reaction.

The gaseous effluent at the top of the 30 upper packed section in the reactor vessel 15 is at a temperature between 700° and 1200°F., and is cooled by a spray of quench liquid in line 38 to about 300°F. Such temperature is above the dew point temperature 35 of the combined gaseous reaction effluent and vaporized quench liquid. The total gaseous effluent is passed into a cyclone separator 39 to remove any solids and is then passed through line 40 to condenser 41 40 to condense the quench liquid. The solids are returned to the upper part of column 15. The mixed vapour/liquid stream is introduced into separator 42 with the condensed quench liquid being passed by pump 43 45 to cooler 44 wherein the liquid is cooled to about 150°F. The cooled quench liquid is then passed to a spray device 38 in reactor 15. The gaseous effluent from separator 42 at about 230°F. is passed through line 45 50 to a separation section illustrated in Figure 2.

The melt withdrawn from the bottom of reactor 15 is at a temperature of from about 700°F. to 1200°F., and is passed through 55 line 36 by pump 37 to the top of dehydrochlorination reactor 35 which is substantially vertical. Dichloroethane which is separated in the separation section is introduced through line 46 at a temperature of about 60 100°F. into the bottom of the dehydrochlorination reactor 35. The dehydrochlorination reactor 35 includes one or more packed sections, generally indicated as 47, to effect intimate and effective contact between 65 the dichloroethane and molten salt. The di-

chloroethane is passed in countercurrent contact with the melt to effect the endothermic dehydrochlorination of the dichloroethane to yield vinyl chloride and hydrogen chloride. The reaction is conducted at a temperature 70 of from 700° to 1200°F., a pressure of 1 to 20 atmospheres, with a residence time of 1 to 60 seconds. The dichloroethane may also flow concurrently downward with the molten salt, in which case the dichloroethane 75 is fed into reactor 15 through a port (not shown) slightly below the level of the entry port from line 36. Barriers (not shown) inside the packing 47 will then be needed to ensure adequate contact between the molten salt and the dichloroethane and to stop the dichloroethane flashing off substantially unaffected.

The gaseous effluent leaving the top of the upper packed section of the dehydrochlorination reactor 35 at a temperature of 85 from 700° to 1200°F. is cooled by means of a spray quench liquid through a spray device 48 to lower the temperature of the gaseous effluent to between 300° to 400°F., 90 thereby eliminating entrained and vaporized salts. The gaseous effluent together with vaporized quench liquid is withdrawn from the upper part of the reactor 35 through line 49 and is passed into a cyclone separator 50 where any solids are removed and returned to the upper part of column 35. The gaseous effluent from separator 50 is passed through line 51 into a condenser 52 where, at a temperature of 150° to 200°F., 95 the quench liquid is condensed. The mixed vapour/liquid stream is thereafter passed into a separator 53, from which the condensed quench liquid is passed through line 54 by pump 55 to heat exchanger 56 wherein the temperature of the quench liquid is lowered to 80° to 120°F. The cooled quench liquid is then passed to a spray device 48 100 in the top of reactor 35. The effluent vapour at 150° to 200°F. withdrawn from the separator vessel 53 is passed through line 57 to the separation section, as described below. The molten salt at the bottom of the reactor 35, which is at a temperature lower than at 105 the inlet to the reactor 35, is withdrawn and passed by a pump 58 through line 59 to the top of the direct heat exchange vessel 20.

The heat exchange vessel 20 comprises one or more packed sections, generally indicated as 60. A portion of the gas withdrawn from the separator 22 is passed through line 27, compressed in a compressor 26, and is introduced into the top of the heat exchange vessel 20 wherein the compressed gas is passed in direct heat exchange contact with the 110 molten salt introduced through line 59. The gas and the molten salt are concurrently passed over the packed sections 60 and are disengaged in the bottom of the heat exchange vessel 20. The gas is cooled by a 115 120 125 130

spray of quench liquid through spray device 61 to eliminate any vaporized or entrained halide salt. A gaseous effluent comprised of the gas introduced through line 27 and 5 the now vaporized quench liquid is withdrawn from vessel 20 and passed into a cyclone separator 62, where any solids are removed from the gaseous effluent. The solids are returned to the bottom of ex- 10 changer 20. The gaseous effluent withdrawn from the separator 62 is passed through line 19 and combined with the gaseous effluent from the oxidation vessel 11 in line 19. The combined gaseous effluent is passed through 15 the heat exchanger 21 to condense the quench liquid. The principal purpose of the heat exchange vessel 20 is to bring the molten salt in line 59 to a constant and desired temperature prior to passing the molten salt 20 through line 10 into the top of the oxidation vessel 11.

Referring now to Figure 2, the reactor effluent from reactor 15 in line 45 comprises vinyl chloride, hydrogen chloride, dichloroethane, ethyl chloride, water and heavier chlorinated hydrocarbons. The reactor effluent is cooled to about 80° to 100°F. in condenser 63, primarily to condense water and heavier chlorinated hydrocarbons. 25 The condensed water and heavier chlorinated hydrocarbons are passed to separator 64 wherein the water and chlorinated hydrocarbons separate into two phases. The water withdrawn from separator 30 for 64 in line 65 is neutralized and stripped of entrained and dissolved chlorinated hydrocarbon in a stripping column (not shown). The chlorinated hydrocarbons are withdrawn 35 from vessel 64 through line 66 and combined with any chlorinated hydrocarbons recovered 40 from the water in the stripping column (not shown) for further processing.

The uncondensed portion of the effluent gaseous stream from the reactor is withdrawn 45 from condenser 63 through line 70 and introduced into an absorption column 71 wherein any acid gases, principally any carbon dioxide present, are removed by any of several well-known acid gas absorption 50 systems. A gaseous effluent is withdrawn from the absorption column 71 through line 72 and is passed into a dryer 73 for removal of residual water.

The effluent vapour in line 57 from the dehydrochlorination reactor 35 (see Fig. 1) 55 is passed through a condenser 79 wherein the effluent vapour is cooled to 80° to 120°F., primarily to condense unconverted dichloroethane which is passed to vessel 80. The unconverted dichloroethane withdrawn 60 from the vessel 80 through line 81 is combined with chlorinated hydrocarbons in line 66. The combined stream is passed through drier 67 and is introduced through line 68 65 into a distillation column 69. The uncon-

densed gaseous effluent in condenser 79 is withdrawn through line 82 and is passed into a dryer 73 wherein the uncondensed gaseous effluent is combined with gaseous effluent in line 72. The dried gas is withdrawn from drier 73 through line 74 to compressor 75, and compressed to 10 to 30 atmospheres. The compressed gas is thereafter passed through line 76 through a heat exchanger 77 and is introduced into the distillation column 69.

The distillation column 69 is operated at temperatures and pressures to produce a gaseous overhead comprised of ethane, ethylene and hydrogen chloride. The vapour emanating from the top of column 69 is cooled and the condensate after separation in a vessel 97, is pumped back into column 69. The gaseous overhead from the vessel 97 is passed via a valve through line 83, heat exchanger 77 and is then introduced through line 32 into the reactor vessel 15, as shown in Figure 1. The column bottoms consisting of chlorinated hydrocarbons are withdrawn from column 69 through line 84, and part of the bottoms is returned to the column 69 by way of heat exchanger 98. The remainder of the bottoms is introduced into a distillation column 85, which is operated at temperatures and pressures to form an overhead primarily comprised of vinyl chloride with minor amounts of impurities. The vapour emanating from the top of column 85 is cooled and condensed, part of the condensate being pumped back to the column 85, while the remainder is passed in line 86 to a purification system (not shown) for the final purification by the elimination of the impurities to produce monomer grade vinyl chloride. The column bottoms are withdrawn from the distillation column 85 through line 87, part of the bottoms being returned to the column 85 by way of heat exchanger 99, while the remainder is introduced into a distillation column 88.

The distillation column 88 is operated at temperatures and pressures to produce an overhead stream consisting of all remaining chlorinated hydrocarbons boiling below dichloroethane. The overhead from the column 88 is cooled and condensed, part of the condensate being pumped back to the column 88, while the remainder is passed through line 89 into a distillation column 90. The column bottoms are withdrawn from column 88 through line 91, part of the bottoms being returned to the column 88 by way of a heat exchanger 100 while the remainder is introduced into a distillation column 92.

The distillation column 90 is operated at temperatures and pressures designed to form an overhead stream comprised substantially of pure ethyl chloride. The overhead is

cooled, and condensed, part of the condensate being pumped back to the column 90, while the remainder is passed through line 93 and is introduced into the reactor 15 5 through line 31, as shown in Figure 1. The bottoms from distillation column 90 consisting largely of dichloroethylenes is withdrawn through line 101, part of the bottoms being returned to the column 90 by way of 10 heat exchanger 102, the remainder being pumped, cooled and withdrawn from the system through line 94.

The distillation column 92 is operated at temperatures and pressures designed to 15 produce an overhead comprised substantially of pure dichloroethane. The overhead is cooled and condensed, part of the condensate being pumped back to the column 92 while the remainder is passed through line 20 95 and is introduced into the dehydrochlorination reactor 35 through line 46, as shown in Figure 1. The bottoms stream from distillation column 92, consisting primarily of trichloroethylene, trichloroethane, 25 perchloroethylene and tetrachloroethane is withdrawn through line 103, part of the bottoms being returned to the column 92 by way of heat exchanger 104, the remainder being pumped cooled and withdrawn from 30 the system through line 96.

The invention is illustrated in the following Example.

EXAMPLE

A molten salt, consisting of 30% potassium chloride and 70% cuprous and cupric chlorides, all by weight, is contacted with air in an oxidation reactor maintained at a temperature of 885°F. at a rate equivalent to addition to the molten salts of 330 cm³ 35 per minute of oxygen.

A molten salt, containing about 2.2 wt percent of copper oxychloride (CuO.CuCl₂), is withdrawn from the oxidation reactor and introduced into a packed chlorination reactor 45 tor maintained at a temperature of 885°F. The molten salt introduced into the reactor is passed counter-currently to an ethane-chlorine feed, the ethane and chlorine being introduced into the reactor at a flow rate of 50 600 cm³/min. and 250 cm³/min., respectively. The overall residence time in the reactor is fifteen seconds.

The effluent withdrawn from the chlorination reactor has the following composition, excluding water and hydrogen chloride:

TABLE I
mol % of C₂H₂ Converted

Component	
C ₂ H ₂	18.2
C ₂ H ₂ Cl	13.4
C ₂ H ₂ Cl ₂	35.6
C ₂ H ₂ Cl ₃	2.0
C ₂ H ₂ Cl ₄	23.6
C ₂ H ₂ Cl ₅	1.7
C ₂ H ₂ Cl ₆	1.2

C ₂ Cl ₄	0.6
CO ₂	1.7
CO	1.4
CH ₄	0.6
Total	100.0
	70

The ethane conversion is 59%, with 96.3% of the ethane converted producing chlorinated hydrocarbons, and the remainder carbon oxides and methane. The chlorine introduced into the reactor is converted to chlorinated hydrocarbons at a 75% rate of conversion and the hydrogen chloride produced *in situ* is converted to 80 chlorine at an 80% rate of conversion.

The 1,2-dichloroethane recovered from the effluent from the chlorination reactor is introduced into a dehydrochlorination reactor at a flow rate of 771 cm³ per minute. 85 The reactor contains the molten salt withdrawn from the chlorination reactor. The molten salt is at a temperature of 849°F. and the total contact time between the molten salt and 1,2-dichloroethane is 4.2 seconds. 90

The gaseous effluent withdrawn from the dehydrochlorination reactor has the following composition, excluding hydrogen chloride and unconverted 95 1,2-dichloroethane:

TABLE II	
Component	mol %
C ₂ H ₂ Cl	99.6
1,1-C ₂ H ₂ Cl ₂	0.1
cis 1,2-C ₂ H ₂ Cl ₂	0.1
C ₂ HCl ₃	0.05
1,1,2-C ₂ H ₂ Cl ₃	0.05
C ₂ Cl ₄	0.1
Total	100.0
	105

The conversion of 1,2-dichloroethane is 47%, with a 99.6% selectivity for vinyl chloride.

It is an advantage of the present invention that a high yield of vinyl chloride can be produced using either ethylene, ethane, or mixtures thereof. It is another advantage of the present invention that dichloroethane can be converted to vinyl chloride 115 product.

WHAT WE CLAIM IS:—

1. A process for the production of vinyl chloride, which comprises passing (a) ethane, ethylene or a mixture thereof, and (b) chlorine, hydrogen chloride, or a mixture thereof, into a first reaction zone, in which is a melt containing at least one chloride of a multivalent metal and the oxychloride of that metal to produce a gaseous effluent including vinyl chloride and 1,2-dichloroethane, withdrawing the gaseous effluent from the first reaction zone and separately recovering vinyl chloride and 1,2-dichloro- 130

- ethane as products therefrom; contacting the recovered 1,2-dichloroethane with a catalyst comprising a melt containing a chloride of the said metal in a second reaction zone 5 wherein 1,2-dichloroethane is dehydrochlorinated to produce an effluent containing vinyl chloride and separating vinyl chloride as product therefrom.
2. A process according to claim 1, where-
10 in the multivalent metal is copper.
3. A process according to claim 1 or 2, wherein the first and second reaction zones are maintained at a temperature of 700° to 1200°F.
- 15 4. A process according to any of claims 1-3 wherein the melt from the first reaction zone, which is heated by exothermic reac-
20 tion in the first zone, contains the chloride of the metal in its lower valency state and is transferred to the second reaction zone, wherein it is cooled by the endothermic de-
hydrochlorination reaction.
- 25 5. A process according to any preceding claim, wherein the melt in at least the first reaction zone contains an alkali metal chloride.
- 30 6. A process according to any preceding claim, wherein ethylene, ethane and hydro-
gen chloride are separated from the gaseous effluent from the first reaction zone and are recycled to the first reaction zone.
- 35 7. A process according to any preceding claim wherein ethyl chloride is separated from the gaseous effluent from the first reaction zone and is recycled to the first reaction zone.
8. A process according to any preceding claim wherein at least a portion of the vinyl chloride free effluent from the second reac-
- tion zone is recycled to the first reaction 40 zone.
9. A process according to any preceding claim wherein prior to separating the vinyl chloride the gaseous effluents from the first and second reaction zones are fractionated 45 to form a gaseous stream primarily comprising ethylene, ethane and hydrogen chloride.
10. A process according to claim 9, wherein the gaseous stream is recycled to the 50 first reaction zone.
11. A process according to any preceding claim, wherein prior to separating the vinyl chloride the gaseous effluents from the first and second reaction zones are com- 55 bined.
12. A process according to any preceding claim wherein the melt is withdrawn from the second reaction zone and contacted in a third reaction zone with a gas containing 50 molecular oxygen to produce the oxychloride of the multivalent metal and the regenerated melt is recycled to the first reaction zone.
13. A process for the production of vinyl chloride, substantially as hereinbefore de- 65 scribed with reference to and as illustrated in the accompanying drawings.
14. A process for the production of vinyl chloride, substantially as described in the Example.
15. Vinyl chloride, made by a process according to any of the preceding claims. 70

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COMPLETE SPECIFICATION
2 SHEETS
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the Original on a reduced scale.
SHEET 1

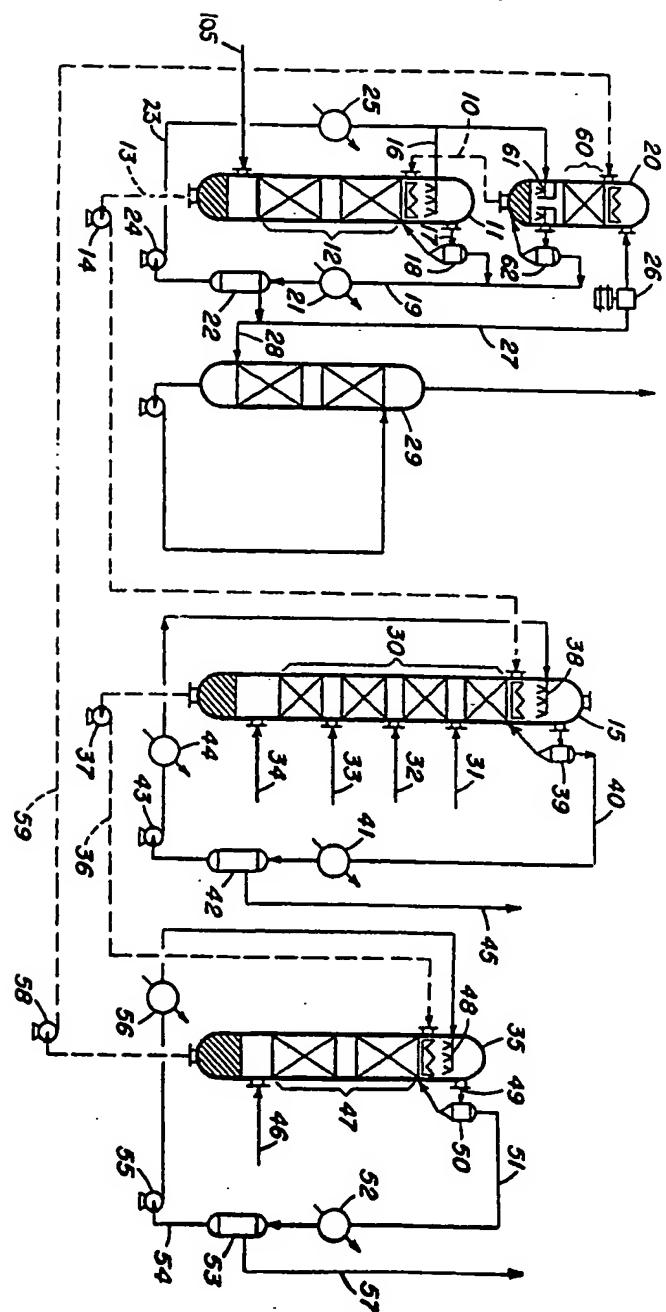


Fig. 1.

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COMPLETE SPECIFICATION

2 SHEETS

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SHEET 2

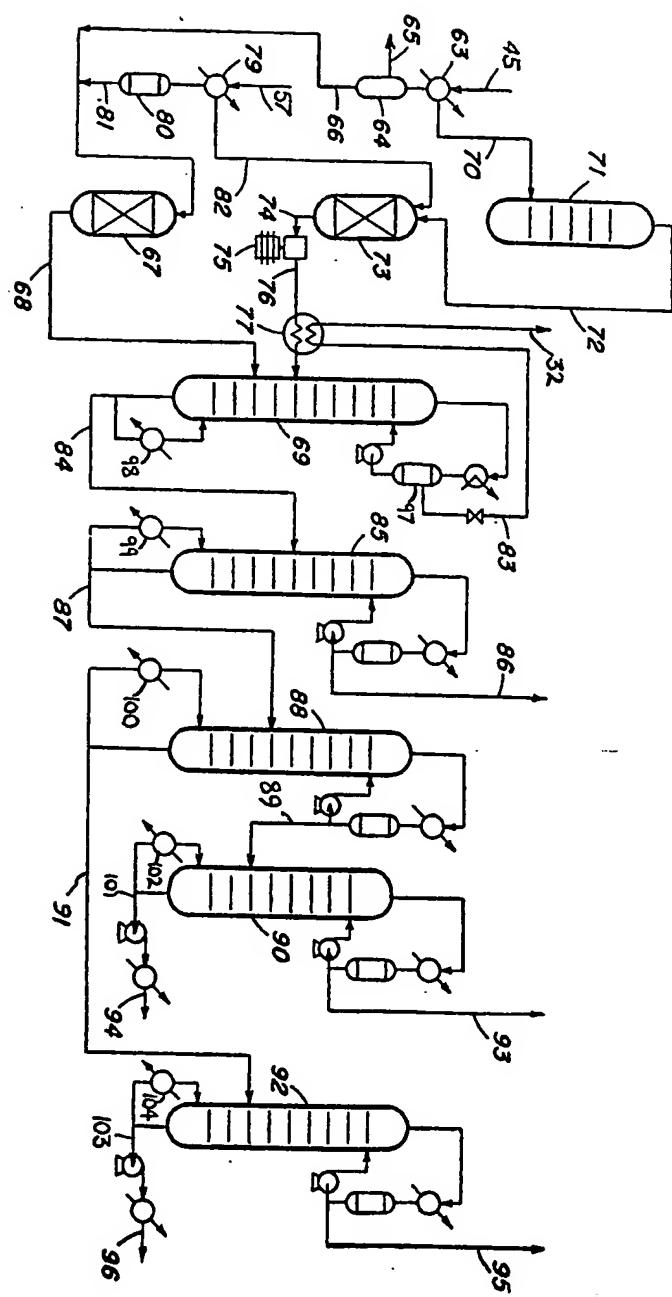


Fig. 2.